

Computer program for centrifugal distortion in asymmetric top rotational spectra

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The electronic computer Besk has previously been applied to the analysis of asymmetric top rotational spectra in the rigid case (1) (2). In the present work the use of Besk has been extended to a first order treatment of centrifugal distortion in such spectra. The program has been tried on a group of Q-branch lines in the spectrum of formaldehyde and has given a good representation of observed distortions. The results obtained are consistent with results obtained previously by other methods.

Method of calculations

As shown e.g. in (3) the influence of centrifugal distortion on the rotational energies may be represented to first order of approximation by an expression of the form

$$W = W_0 + D_1 W_0^2 + D_2 J(J+1) W_0 + D_3 J^2(J+1)^2 + D_4 J(J+1) \langle P_a^2 \rangle + \\ + D_5 \langle P_a^4 \rangle + D_6 W_0 \langle P_a^2 \rangle \quad [1]$$

where W_0 is the rigid rotor frequency, P_a is the component of angular momentum along one principal axis of the molecule, and the brackets $\langle \rangle$ denote average values for the energy level in question.

The distorted value of a line frequency is obtained as the difference between two equations of the form [1]. If a sufficient number of rotational lines are known, this formula gives a system of equations from which the constants D_1 to D_6 may be determined. For this purpose, however, one must know the values of W_0 , $\langle P_a^2 \rangle$ and $\langle P_a^4 \rangle$ for all levels involved. These values may all be calculated from known values of the rotational constants A , B and C of the molecule.

The general procedure for the application of formula [1] is therefore to start from values of A , B and C , obtained from reasonably undistorted lines or from suitable approximation methods, and to calculate W_0 , $\langle P_a^2 \rangle$, and $\langle P_a^4 \rangle$ for all levels of interest. The differences $\Delta W_0 = \nu_0$, ΔW_0^2 etc. are then formed, giving a system of equations for the D_i , which is finally solved by the least squares method.

The present program consists of three parts. Part 1 calculates the reduced energies, $E(b)$, together with $\langle P_a^2 \rangle$ and $\langle P_a^4 \rangle$ for all levels of each sub-matrix involved in the transitions considered. Part 2 calculates the complete energies W_0 for the particular levels involved, and sets up the resulting system of equations. Part 3, finally, gives the solution of this system.

Details of the program

Part 1 of the program sets up the elements of the energy sub-matrix considered, using the asymmetry parameter $b = (C - B)/(2A - B - C)$ and calculates the reduced energies $E(b)$ by means of the continued fraction method (4). The matrix representation employed is diagonal in the prolate symmetric rotor case ($b = 0$). The calculations of $E(b)$ start from approximate input values and proceed to a relative accuracy better than one part in 10^{11} .

A difficulty often encountered in calculating reduced energies by the continued fraction method is sporadic divergence of the fractions for special values of the asymmetry parameter. This situation may always be remedied by choosing a development starting with another diagonal element in the matrix. The present program considers all developments for each case simultaneously, and selects the one giving the best convergence. This procedure results in a comparatively simple and effective program avoiding the administration procedures for changing the development form. Changes in the approximations tried are at first limited to absolute values smaller than unity. Refinements are then calculated by the "regula-falsi" method.

After evaluating all $E(b)$'s for one sub-matrix and storing the results in the memory, the program proceeds to calculate the elements of the transformation matrix T , which diagonalises the energy matrix. The transformation T is then applied to the diagonal matrices K^2 and K^4 , which represent P_a^2 and P_a^4 in the original system. The diagonal elements of the matrices thus transformed give the desired averages $\langle P_a^2 \rangle$ and $\langle P_a^4 \rangle$. These are printed in an output table together with corresponding values of $E(b)$. If desired the program then proceeds automatically with other matrices or other b -values.

The T -matrix is evaluated according to the procedure given by King, Hainer, and Cross (4). This requires a very high degree of accuracy in the values of the reduced energies and in the arithmetic operations involved. A small error in the first elements of a column may grow to considerable magnitude at the bottom of the column by successive multiplications with elements in the order of K^2 , where K takes on alternate integer values up to J . These difficulties are especially pronounced near the symmetric case $b = 0$.

In the present program the accuracy obtainable is limited by the word-length of the machine, which is 40 binary digits. Calculations are performed in a floating-point manner conserving the relative accuracy as far as possible. For future work an improved program using the double word-length is being planned.

In the case of formaldehyde, which is a nearly symmetric rotor, the straight-forward calculation of T could not be used for $J > 13$. For higher J 's errors occurred in $\langle P_a^2 \rangle$ and $\langle P_a^4 \rangle$, which could be observed by checking the traces of the matrices. The errors in the T -elements occurred at first far below the main diagonal. An improvement was obtained by setting such elements equal to zero, as soon as they could be estimated to be unimportant. This procedure gave satisfactory results up to $J = 17$ for the formaldehyde case.

Part 2 is a straight-forward arithmetic and administrative program evaluating the coefficients of the desired system of equations. Part 3 is a standard program for the solution in Besk of over-determined systems of linear equations by the least squares method.

Table 1

Transition	Observed frequency Mc	Rigid rotor frequency Mc	Centrifugal distortion Mc	Calculated distortion Mc
2 _{1,2} -2 _{1,1}	14488.65	14488.22	-0.43	-0.56
3 _{1,3} -3 _{1,2}	28974.85	28972.17	-2.68	-2.62
4 _{1,4} -4 _{1,3}	48284.60	48276.76	-7.84	-7.69
5 _{1,5} -5 _{1,4}	72409.35	72391.71	-17.64	-17.74
7 _{2,6} -7 _{2,5}	8884.87	8871.95	-12.92	-13.19
8 _{2,7} -8 _{2,6}	14726.74	14702.20	-24.54	-24.70
9 _{2,8} -9 _{2,7}	22965.71	22922.12	-43.59	-43.39
14 _{3,12} -14 _{3,11}	7892.03	7834.86	-57.17	-57.04
15 _{3,13} -15 _{3,12}	11753.13	11662.68	-90.45	-90.43
16 _{3,14} -16 _{3,13}	17027.60	16888.33	-139.27	-139.34
17 _{3,15} -17 _{3,14}	24068.31	23859.09	-209.22	-209.22

Practical results

The program has been tried on a group of eleven branch lines in the microwave spectrum of formaldehyde. These lines were reported by Lawrance and Strandberg (5), who accounted for the centrifugal distortion by means of a semi-classical method. The distortions involved are comparatively large, ranging from 0.4 Mc for $J=2$ to 209 Mc for $J=17$. Lawrance and Strandberg also considered six lines of higher J -values, but for reasons explained above these could not be included in the present treatment.

The results obtained for the individual lines are shown in Table 1, which gives observed frequencies (ν), calculated rigid rotor frequencies (ν_0), centrifugal distortions ($\nu - \nu_0$), and distortions calculated from eq. 1 with the constants obtained as results from Besk.

The rotational constants used for the rigid rotor case are taken from (5) and (6) and are:

$$\begin{aligned} A &= 282.106 \text{ kMc} \\ B &= 38.83407 \text{ kMc} \\ C &= 34.00437 \text{ kMc} \end{aligned}$$

The distortion constants for eq. 1 derived by Besk are:

$$\begin{aligned} D_1 &= -0.28627 \cdot 10^{-6} & (\pm 0.039 \cdot 10^{-6}) \\ D_2 &= 0.12209 \cdot 10^{-4} & (\pm 0.028 \cdot 10^{-4}) \\ D_4 &= -0.46625 \cdot 10^{-3} & (\pm 0.081 \cdot 10^{-3}) \\ D_5 &= 0.14253 \cdot 10^{-1} & (\pm 0.047 \cdot 10^{-1}) \\ D_6 &= 0.15399 \cdot 10^{-3} & (\pm 0.022 \cdot 10^{-3}) \end{aligned}$$

The constant D_3 (corresponding to D_7) drops out from the equations for the Q-branch lines. The uncertainties given in parenthesis are those pertaining to the

least squares solution of the equation system. They are not independent of each other, and higher accuracies for the D_i 's should be used in calculating the individual distortions.

From the D_i 's one can derive a value for the distortion constant D_{JK} corresponding to the $J(J+1)K^2$ -term in the symmetric top case. The relations between the various sets of constants are given in ref (3). The resulting value is:

$$D_{JK} = 1.18 \text{ Mc.}$$

This may be compared to the value $D_{JK} = 1.31 \text{ Mc}$ obtained in ref. (6) from a symmetric top approximation to the R-branch lines. Since the accuracy is not very high in neither case, the agreement may be considered satisfactory.

As mentioned above an improved program with better accuracy will be tried later on, and it is hoped that this will make possible the consideration of all the lines observed. It has therefore not been considered worthwhile to proceed further with the analysis at present. Otherwise, some minor adjustments in the rigid rotor rotational constants should be tried, and the procedure be repeated for a best fit.

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REFERENCES

- (1) G. ERLANDSSON, Arkiv för Fysik, 9, 399 (1955).
- (2) G. ERLANDSSON, Arkiv för Fysik, 10, 65 (1955).
- (3) D. KIVELSON and B. WILSON JR., J. Chem. Phys. 20, 1575 (1952).
- (4) G. KING, R. M. HAINER, and P. C. CROSS, J. Chem. Phys. 11, 27 (1943).
- (5) R. B. LAWRENCE and M. W. P. STRANDBERG, Phys. Rev. 83, 363 (1951).
- (6) G. ERLANDSSON, J. Chem. Phys. 25, 579 (1957).

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